

**METHOD FOR FORMING SIO₂ BY CHEMICAL VAPOR
DEPOSITION AT ROOM TEMPERATURE**

Cross-reference to related application

This application claims benefit of provisional application 90/215,381, filed June 29, 2000 and incorporated herein by reference. The U.S. government has a paid-up license in this invention and the right in limited circumstances to require the patent owner to license to others on reasonable terms as provided for by the terms of contract no. F49620-99-1-0081, awarded by the United States Department of Energy.

Background of the Invention

Chemical vapor deposition (CVD) is one of the most widely practiced thin film deposition techniques. Advances in CVD technology have fueled the deployment of many new technologies, including silicon microelectronic processing. One of the key goals for the fabrication of future silicon devices is lower deposition temperatures. These low growth temperatures will limit interlayer and dopant diffusion and facilitate the use of temperature sensitive substances such as polymers or biological materials.

The chemical vapor deposition of SiO₂ is ubiquitous in silicon device fabrication. SiO₂ CVD films compete effectively with thermal SiO₂ that is formed by the reaction of oxygen with the silicon substrate at 900-1200 K. SiO₂ CVD is performed at various temperatures that can be significantly lower than the required temperatures for thermal SiO₂ growth. At high temperatures of ~1200 K, excellent SiO₂ films with properties close to thermal SiO₂ can be grown using the reaction SiH₂Cl₂ + 2NO → SiO₂ + 2N₂ + 2HCl. At medium temperatures of ~900-1000 K, very reasonable SiO₂ dielectric films are deposited using tetraethyl orthosilicate (TEOS) decomposition. Several earlier investigations have reported the kinetics of SiO₂ CVD using SiCl₄ and H₂O. These studies observed efficient SiO₂ CVD only at temperatures greater than 900 K. At fairly low temperatures of ~500-700 K, SiO₂ films with a lower density than thermal SiO₂ can be deposited using the reaction SiH₄ + O₂ → SiO₂ + 2H₂O.

SiO₂ deposition at temperatures as low as room temperature has been the focus of recent research. Plasma processing is often used to lower film deposition temperatures.

However, the drawbacks to plasma processing are particle contamination, surface damage from the energetic plasma species and high interface defect density. The use of novel molecular precursors has also been explored for low temperature SiO₂ growth. However, these precursors are usually expensive, and the SiO₂ films deposited with these precursors have not been device quality.

Amine catalysts have been used for the attachment of chlorosilanes and organosilanes to silica surfaces. See C. P. Tripp and M. L. Hair, J. Phys. Chem. 97, 5693 (1993) and J. P. Blitz et al., J. Amer. Chem. Soc. 109, 7141 (1987). The use of a catalyst has also recently been reported for SiO₂ atomic layer deposition (ALD) using sequential surface reactions. These SiO₂ ALD investigations used either pyridine (C₅H₅N) or ammonia (NH₃) as the catalyst during sequential exposures to SiCl₄ and H₂O. See J. W. Klaus, O. Sneh, A. W. Ott and S. M. George, Surface Review & Letters 6, 435 (1999) and J. W. Klaus, O. Sneh, A. W. Ott and S. M. George, Science 278, 1934 (1997). These previous studies demonstrated that Lewis base molecules can catalyze SiO₂ ALD at room temperature. Recent *ab initio* theoretical calculations have confirmed the catalytic effect of NH₃ on the SiCl₄ and H₂O half-reactions occurring during SiO₂ ALD. Y. Okamoto, J. Phys. Chem. B 103, 11074 (1999).

Brief Description of the Drawings

Figure 1 is a graphical depiction illustrating the sequencing of reactants and catalyst addition for Example 1.

Figure 2 is a graph of SiO₂ film thickness deposited by 30 consecutive NH₃/SiCl₄ pulses at 600 mTorr and 318 K versus NH₃ pressure under the conditions of Example 2.

Figure 3 is a graph of NH₃ thickness on the hydroxylated SiO₂ surface at 318 K versus NH₃ pressure under the conditions of Example 2.

Figure 4 is a graph of SiO₂ film thickness deposited by 30 consecutive NH₃/SiCl₄ pulses at 100 mTorr and 318 K versus H₂O pressure under the conditions of Example 3.

Figure 5 is a graph of H₂O thickness on a hydroxylated SiO₂ surface at 318 K versus H₂O pressure under the conditions of Example 3.

Figure 6 is a graph of SiO₂ film thickness deposited by 30 consecutive NH₃/SiCl₄ pulses at 600 mTorr H₂O, 150 mTorr NH₃ and 318 K versus SiCl₄ pulse length under the conditions of Example 4.

Figure 7 is a graph of total SiO₂ film thickness deposited versus number of SiCl₄

pulses at 100 mTorr NH₃, 300 mTorr H₂O and 318 K under the conditions of Example 4.

Figure 8 is an atomic force microscope image of a SiO₂ film deposited on Si(100) by 500 consecutive NH₃/SiCl₄ pulses at 600 mTorr H₂O, 600 mTorr NH₃ and 318 K under the conditions of Example 5.

Figure 9 is a graph of SiO₂ film thickness deposited by 30 consecutive NH₃/SiCl₄ pulses at 600 mTorr H₂O and 150 mTorr NH₃ versus substrate temperature under the conditions of example 6.

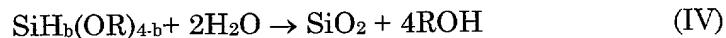
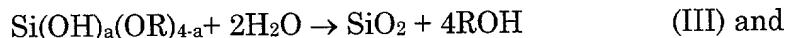
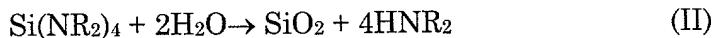
Summary of the Invention

This invention is a chemical vapor deposition process for forming a SiO₂ layer on a substrate comprising reacting water with a silicon precursor compound having the structure SiX₄, Si(NR₂)₄, Si(OH)_a(OR)_{4-a} or SiH_b(OR)_{4-b} wherein each R is an alkyl group, each X is independently a halogen atom, and a and b are numbers from 0-4, in the presence of the substrate at a temperature of between about 290 K and 350 K and in the presence of ammonia or a Lewis base that is a gas under the conditions of the chemical vapor deposition process.

This process permits the formation of high quality SiO₂ coatings on various substrates, most notably on a silicon substrate, using a low temperature process. The process is easily controllable to form conformal SiO₂ layers of a desired thickness. Lower deposition temperatures are particularly important to limit interlayer and dopant diffusion as thin film device sizes approach nanoscale dimensions.

Detailed Description of the Invention

In this invention, an SiO₂ layer is formed on a substrate by the reaction of water with a silicon precursor compound. The silicon precursor compound has the structure SiX₄, Si(NR₂)₄, Si(OH)_a(OR)_{4-a} or SiH_b(OR)_{4-b} wherein each R is an alkyl group, each X is independently a halogen atom, and a and b are numbers from 0-4. X is preferably chloride ion. R is preferably a C₁-C₄ alkyl such as methyl, ethyl, n-propyl, isopropyl, n-butyl, t-butyl or sec-butyl. a and b are each preferably from 0-3, more preferably from 0-2 and most especially 0. SiCl₄ and tetraethyl orthosilicate (TEOS, where each R is ethyl) are especially preferred silicon precursors. The overall reaction is represented by one or more of the (unbalanced) equations



The substrate can be any substrate on which an SiO_2 layer can be deposited. A highly preferred substrate is silicon, especially an $\text{Si}(100)$ wafer. In addition to applications in manufacturing semiconductor devices, low temperature SiO_2 CVD may be used to deposit insulating and protective SiO_2 coatings on a variety of materials, including thermally sensitive materials such as polymers and biological materials. Among such other substrates are nitrides such as aluminum nitride, boron nitride or silicon nitride; oxides such as alumina, titania, or zeolites, metals, carbides such as titanium carbide, boron carbide, silicon carbide, tungsten carbide, and the like. In most cases, the SiO_2 layer will become chemically bound to the substrate through oxygen atoms on the substrate surface.

The catalyst is ammonia or a Lewis base that is a gas under the conditions of the reaction. The Lewis base preferably has a nitrogen atom. Those having H-bond strengths towards Lewis acid sites similar to ammonia and pyridine are especially suitable. Among such catalysts are pyridine, primary, secondary or tertiary amines such as monoalkyl amines (ethyl amine, n-propyl amine, n-butyl amine, t-butyl amine and the like); dialkyl amines such as dimethyl amine, diethyl amine, di-n-propyl amine, methyl ethyl amine and the like) and trialkyl amines (trimethyl amine, triethyl amine and the like). Ammonia is most preferred on the basis of catalytic activity and ease of use.

In accordance with the invention, the foregoing reaction is conducted in a chemical vapor deposition process. In general, this process comprises subjecting the substrate to the reactant under conditions of temperature and pressure so that the reactants and catalyst are in the gaseous state. The reactants react on the surface of the substrate to form an SiO_2 layer on its surface. At the temperature range of interest, 290-350K, especially 313-333K, pressures are selected so that the reactants assume a gaseous state. In general, the substrate is contacted with reactants at a pressure that is preferably less than 50 Torr,

more preferably less than 10 Torr and even more preferably less than 5 Torr. Thus, the process is generally conducted within an evacuated chamber into which the reactants and catalysts can be fed under controlled subatmospheric pressures. The reaction vessel is preferably adapted to be evacuated to low pressures such as 1×10^{-6} Torr, preferably 1×10^{-7} Torr, especially 1×10^{-8} Torr. Suitable such equipment is described in A. W. Ott, J. W. Klaus, J. M. Johnson and S. M. George, Thin Solid Films 292, 135 (1996), incorporated herein by reference.

The chemical vapor deposition process includes the simultaneous addition of the reactants, or at least one of the reactants and the catalyst, so that some mixing occurs in the vapor phase. Typically, the silicon precursor is added simultaneously with water or the catalyst, preferably both. A preferred mode of addition is to introduce water vapor continuously or over relatively long periods. During the water addition, catalyst and silicon precursor are added intermittently in "pulses" of short duration. In this manner, there are periods of time in which only water is being introduced into the reaction, and other periods of time in which water and catalyst are being added simultaneously and still other periods of time in which water and the silicon precursor (and still more preferably, the catalyst) are added simultaneously. This permits the surface of the substrate to first become coated with a thin layer of water molecules, which are then coated with a thin layer of catalyst molecules, and then with a thin layer of the silicon precursor, at which point the reaction between the water and silicon precursor takes place, forming a very thin SiO_2 layer. A certain amount of mixing of the reactants and/or catalyst will occur in the vapor phase, and a certain amount of simultaneous deposition of these materials onto the substrate will occur. Repeated sequential applications of the reactants and catalyst form or increase the thickness of the layer. It is believed that a contiguous SiO_2 layer may be created from "islands" of SiO_2 that are formed during the first or first several applications of the reactants and catalysts, and which grow and are joined together during subsequent applications of the reactants and catalysts.

In an especially preferred method, water vapor is used not only as a reactant, but also as purge stream that helps to flush away excess quantities of the catalyst and silicon precursor as well as by-products of the reaction. In this especially preferred method, water vapor can be introduced continuously into the reactor, with the catalyst and silicon precursor being "pulsed" (i.e., added to the reactor under pressure for an interval of time) into the reactor periodically. The catalyst and silicon precursor "pulses" are preferably

performed with the catalyst being introduced first, followed by the silicon precursor. In an especially preferred process, the catalyst is pulsed into the reactor, and the silicon precursor is pulsed into the reactor near the end of the catalyst pulse, so that the silicon precursor is introduced simultaneously with the last portion of the catalyst pulse. Between pulses of catalyst/silicon precursor, it is preferred to purge the reactor with water or an inert gas, in order to remove excess raw materials and by-products of the reaction.

The amount of reactants and catalyst that are introduced in a given addition will depend on the pressure and the length of time of the addition. For catalyst and silicon precursor additions, it has been found that most efficient SiO₂ layer growth is achieved when each addition is sufficient to deposit approximately a monolayer of molecules on the surface of the substrate. Adding greater amounts contributes little to the rate of SiO₂ growth and may tend to cause the SiO₂ layer to become less uniform, whereas adding substantially less tends to slow the rate of SiO₂ layer growth.

For any particular apparatus and substrate, suitable pulse lengths and pressures can be determined empirically. A preferred set of conditions includes adding H₂O in pulses or continuously until an H₂O partial pressure of about 50 to about 5,000 mTorr, especially 100 to 500 mTorr, is achieved. Catalyst pulsing is preferably done to achieve a catalyst partial pressure of about 50 to about 2500 mTorr, preferably about 50 to about 1000 mTorr, more about 100 to about 500 mTorr, especially about 100 to 300 mTorr. Silicon precursor pulsing is preferably done to achieve silicon precursor partial pressure of from about 2 to about 2500 mTorr, preferably from about 5 to about 500 mTorr, more preferably from about 5 to about 200 mTorr.

The process is continued until a film of SiO₂ of the desired thickness is deposited onto the substrate. The film thickness may range from about 10 nm to any desired thickness, provided that the deposition process is repeated enough times. The process of the invention is particularly suitable for forming layers of from about 50 to about 1000 nm.

HCl, dialkylamines and/or alcohols are produced when the water reacts with the various silicon precursors. The catalyst may then form reaction by-products, particularly ammonium chlorides when HCl reacts with NH₃. These by-products may become affixed to the surface of the growing SiO₂ film. Purging the reactor between reaction sequences tends to remove these by-products as well as other impurities that may form. Thus, it is preferred to separate each sequence of reactions with a purge of an inert gas, or preferably, water vapor. The purge may continue for up to 1 minute or more, depending on the

particular conditions and design of the reactor, but often a purge of from about 1 to about 50 seconds, especially from about 10 to about 50 seconds, is adequate to remove most of the by-products and form a good quality film.

The following examples are provided to illustrate the invention, but are not intended to limit its scope. All parts and percentages are by weight unless otherwise indicated. These examples are conducted in an apparatus as described in A. W. Ott, J. W. Klaus, J. M. Johnson and S. M. George, Thin Solid Films 292, 135 (1996). The apparatus includes a sample load lock chamber, a central deposition chamber, and an ultra high vacuum chamber for surface analysis. The central deposition chamber is designed for automated dosing of gas phase precursors under a wide variety of conditions. The deposition chamber is pumped with either a 175 l/s diffusion pump equipped with a liquid N₂ trap or two separate liquid N₂ traps backed by mechanical pumps. This chamber has a base pressure of 1x10⁻⁷ Torr. The central deposition chamber contains an in situ spectroscopic ellipsometer (J. A. Woolam Co. M-44) that collects ellipsometric data simultaneously at 44 visible wavelengths. The ellipsometer is mounted on ports positioned at 80° with respect to the surface normal. Gate valves on the ports protect the birefringent-free ellipsometer windows from deposition during film growth. The surface analysis chamber houses a UTI-100C quadrupole mass spectrometer and is pumped by a 210 l/s turbo pump to a base pressure of 1 x 10⁻⁸ Torr. Mass spectrometric analysis of the gases in the central deposition chamber can be performed using a controlled leak to the surface analysis chamber.

The sample substrates were 0.75 x 0.75 inch Si(100) wafers. The Si(100) samples were p-type, boron-doped with a resistivity of $\rho = 0.1 - 0.4 \Omega\text{cm}$. A 3000 Å Mo film deposited on the backs of the samples was used for resistive heating to >1100 K. The Si(100) samples were cleaned in HF to remove the native oxide. The Si(100) surface was further cleaned in vacuum by annealing at 875 K for 1 minute. This anneal was followed by a high frequency H₂O plasma discharge at 300 K to hydroxylate the surface and remove surface carbon contamination. The cleaning procedure leaves a very thin SiO₂ film on the Si(100) substrate.

Example 1. SiO₂ deposition onto Si(100) wafers

SiO₂ deposition experiments were performed using the reaction sequence illustrated in Fig. 1. A steady-state pressure of H₂O was maintained in the central deposition chamber

by continuously flowing H₂O through the chamber. The H₂O pressure was controlled by varying the conductance between the chamber and the pumps using an in-line butterfly valve. The NH₃ catalyst and SiCl₄ precursor were then introduced into the deposition chamber using automated valves. The NH₃ pressure was controlled using the regulator on the NH₃ gas cylinder. The SiCl₄ precursor was pulsed into the deposition chamber after establishing the NH₃ pressure. The SiCl₄ exposure was defined by opening the SiCl₄ automated valve for 50 ms. This SiCl₄ pulse yielded a peak SiCl₄ pressure of ~5 mTorr as measured by a capacitance manometer on the deposition chamber. Following the NH₃/SiCl₄ pulse sequence, the NH₃ and SiCl₄ valves were closed, and the continuous H₂O flow purged the chamber. A purge time of 20-60 secs was required to reestablish the steady-state H₂O pressure.

The NH₃ catalyst can form complexes with HCl reaction product to yield NH₄Cl salt. NH₄Cl has a vapor pressure of 4×10^{-5} Torr at 300 K. The H₂O purge also removed the NH₄Cl from the SiO₂ surface and the chamber walls.

The SiO₂ film thickness was evaluated after 30 identical NH₃/SiCl₄ pulses using the in situ spectroscopic ellipsometer. Bulk SiO₂ optical constants were initially assumed because the refractive index of very thin films is difficult to determine. The accuracy of this assumption was tested by collecting ex situ data on a 1000 Å thick SiO₂ film at multiple angles of incidence. This examination permits an accurate determination of the SiO₂ optical constants. The measured index of refraction of $1.43 \pm .03$ for the catalyzed SiO₂ CVD films agrees with the refractive index of 1.46 for dense thermal SiO₂ films.

Example 2. Comparison of film growth with and without NH₃ catalyst

When example 1 is repeated without using any NH₃ catalyst, no SiO₂ CVD film growth was observed at any temperature between 300 - 700 K for SiCl₄ and at H₂O pressures as high as to 2 Torr. In contrast, the addition of a small amount of NH₃ initiated immediate SiO₂ growth at 313-333 K. The effect of the NH₃ catalyst was quantified by measuring the SiO₂ film thickness deposited by 30 consecutive NH₃/SiCl₄ pulses at 318 K versus NH₃ pressure. These in situ spectroscopic ellipsometry measurements are shown in Fig. 2. The solid line is intended only to guide the eye. The steady-state H₂O pressure was 600 mTorr and the SiCl₄ pulse length was fixed at 50 ms for the results shown in Fig. 2. H₂O was allowed to purge the deposition chamber for 20 seconds between each NH₃/SiCl₄

pulse. The H₂O/NH₃/SiCl₄ reaction cycle occurred with the following sequence: Flow H₂O (600 mTorr) / Flow NH₃ (0 - 3 Torr) / Pulse SiCl₄ (50 ms) / Close SiCl₄ and NH₃ valves / Flow H₂O (20 sec). Figure 2 shows that the deposited SiO₂ film thickness increases rapidly with increasing NH₃ pressures up to 3.0 Torr. NH₃ pressures > 3.0 Torr were not attainable during the reaction cycles when the deposition chamber was connected to the pumps. Given the total time required for the 30 NH₃/SiCl₄ pulses, the catalyzed SiO₂ CVD rates varied from 0.4 Å /min at 50 mTorr NH₃ to 8.1 Å /min at 3.0 Torr NH₃.

The data in Figure 2 suggests that enhancement of SiO₂ CVD with NH₃ pressure results from a progressive increase in NH₃ coverage with NH₃ pressure. In situ ellipsometry was used to measure the NH₃ coverage on a fully hydroxylated SiO₂ surface. A refractive index of $n = 1.325$ was utilized based on the previous measurements for liquid ammonia at 289 K as reported by W.L. Jolly and C. J. Hallada, "Liquid Ammonia" in *Non-Aqueous Solvent Systems*, ed. by T.C. Waddington; Academic Press: London, 1965, Chapter 1. Figure 3 displays the NH₃ coverage versus NH₃ pressure at 318 K. For NH₃ pressures < 1 Torr, the NH₃ thickness increases rapidly with pressure. In this monolayer regime, the NH₃ molecules are adsorbing strongly to surface SiOH* groups. (As used herein, an asterisk * denotes an active surface species.) The NH₃ thickness increases much more slowly at NH₃ pressures > 1 Torr. At these pressures, the NH₃ molecules are adsorbing less strongly onto themselves and form a NH₃ multilayer.

The Brunauer-Emmett-Teller (BET) adsorption model was used to fit the ellipsometric data. See J. B. Hudson, *Surface Science: An Introduction*; Butterworth-Heinemann: Troy, New York, 1992. The BET model relates NH₃ coverage to: τ_1 , the NH₃ lifetime on the silanol surface; τ_2 , the NH₃ lifetime on the ammonia multilayer; n_0 , the NH₃ density in one complete monolayer; and I , the incident NH₃ flux. A molecular density in the first monolayer of $n_0 = 7.6 \times 10^{14}$ molecules/cm² was obtained from the density of liquid ammonia. The density of liquid ammonia also yields a thickness of 3.6 Å for the NH₃ monolayer. The BET fit is shown as the solid line in Fig. 3. The NH₃ lifetimes of $\tau_1 = 3 \times 10^{-6}$ s and $\tau_2 = 7 \times 10^{-9}$ s at 318 K were obtained from this fit.

Additional ellipsometric measurements of the NH₃ coverage versus NH₃ pressure at different temperatures were consistent with an adsorption energy of $E = 9.4 \pm 0.8$ kcal/mol and a desorption preexponential of $v_0 = 1.0 \times 10^{12 \pm 0.8}$ s⁻¹ for NH₃ on the silanol surface. Assuming a desorption preexponential of $v_0 = 1.0 \times 10^{12}$ s⁻¹, the NH₃ lifetime of $\tau_2 = 7 \times 10^{-9}$ s

yielded an adsorption energy of 5.6 kcal/mol for NH₃ on the ammonia multilayer. This adsorption energy is in excellent agreement with the heat of vaporization of 5.58 kcal/mol for ammonia at the boiling point.

Figure 2 displays two SiO₂ CVD growth regimes versus NH₃ pressure. For NH₃ pressures < 1 Torr, the SiO₂ film thickness deposited by 30 NH₃/SiCl₄ pulses increases nearly linearly with NH₃ pressure. In contrast, the SiO₂ film thickness deposited by 30 NH₃/SiCl₄ pulses increases more slowly for NH₃ pressures > 1 Torr. This SiO₂ growth behavior is explained by the NH₃ adsorption isotherm at 318 K displayed in Fig. 3.

The NH₃ adsorption isotherm shown in Fig. 3 exhibits a turnover at 1 Torr. At this pressure, the NH₃ molecules have nearly completed the first monolayer formation by binding to most of the SiOH* surface species. At pressures > 1 Torr, the NH₃ molecules adsorb less strongly as a result of NH₃ multilayer formation. This decrease in the NH₃ adsorption efficiency at > 1 Torr is directly reflected by the SiO₂ deposition versus NH₃ pressure.

Example 3. Dependence of SiO₂ CVD on H₂O Exposure

The dependence of catalyzed SiO₂ CVD on the H₂O exposure was examined by measuring the SiO₂ film thickness deposited by 30 consecutive NH₃/SiCl₄ pulses at 318 K for various H₂O pressures. The NH₃ pressure was 100 mTorr. Each SiCl₄ pulse was defined by opening the automated valve for 50 ms to produce a peak SiCl₄ pressure of ~ 5 mTorr in the chamber. The H₂O was allowed to purge the chamber for 20 seconds between each NH₃/SiCl₄ pulse.

Figure 4 shows that the SiO₂ deposited by 30 NH₃/SiCl₄ pulses increases rapidly with increasing H₂O pressure from 150 mTorr to 1.5 Torr. The solid line is shown only to guide the eye. Based on the time needed for the 30 NH₃/SiCl₄ pulses, the catalyzed SiO₂ CVD rate varied from 0.12 Å/min at 150 mTorr H₂O to 3.0 Å/min at 1.5 Torr H₂O.

The enhancement of the SiO₂ CVD versus H₂O pressure results from a progressive increase in the H₂O coverage with H₂O pressure. In situ ellipsometry was used to measure the H₂O coverage on a fully hydroxylated SiO₂ surface. A refractive index of $n = 1.33 \pm .05$ was determined for the H₂O multilayer. Figure 5 displays the H₂O coverage on the silanol surface versus static H₂O pressure at 318 K. For H₂O pressures < 500 mTorr, the H₂O thickness increases rapidly with pressure. In this monolayer regime, the H₂O molecules are adsorbing strongly to surface SiOH* groups. The H₂O thickness increases more slowly at

H_2O pressures > 500 mTorr. At these H_2O pressures, the H_2O molecules are adsorbing less strongly onto themselves and form a H_2O multilayer.

The Brunauer-Emmett-Teller (BET) adsorption model was again utilized to fit these ellipsometry results. This fit is displayed as the solid line in Fig. 5. From this data and measurements at additional temperatures, the BET model yielded a H_2O surface adsorption energy of $E = 12.1 \pm 0.9$ kcal/mol and a desorption preexponential of $v_0 = 3.3 \times 10^{14 \pm 0.9} \text{ s}^{-1}$ on the silanol surface at 318 K. A comparison of Figs. 4 and 5 indicates that the SiO_2 CVD rate and the H_2O surface coverage both increase versus H_2O pressure. This correspondence continues in the H_2O multilayer regime at H_2O pressures > 500 mTorr. In contrast to the NH_3 dependence, the dependence of the catalyzed SiO_2 CVD on H_2O pressure displayed in Fig. 4 first increases slowly versus H_2O pressure and then increases more rapidly at H_2O pressures > 500 mTorr.

Example 4. Dependence of SiO_2 CVD on SiCl_4 Exposure

Ellipsometric measurements also examined the dependence of the catalyzed SiO_2 CVD on SiCl_4 exposure. Figure 6 displays the SiO_2 film thickness deposited by 30 consecutive $\text{NH}_3/\text{SiCl}_4$ pulses at 318 K versus SiCl_4 pulse length. The SiCl_4 peak pressure during each SiCl_4 pulse varied from ~ 5 mTorr for 50 msec pulse lengths to ~ 150 mTorr for 1000 msec pulse lengths. The H_2O pressure was 600 mTorr and the NH_3 pressure was 150 mTorr. The H_2O was allowed to purge the system for 20 seconds between each $\text{NH}_3/\text{SiCl}_4$ pulse.

Figure 6 indicates that there are two distinct SiO_2 CVD growth regimes as the SiCl_4 pulse length is varied from 10 msec to 1000 msec. The solid line connects the points and is displayed to direct the eye. SiCl_4 pulse lengths < 300 msec result in SiO_2 deposition that is directly proportional to the SiCl_4 pulse length. In contrast, SiCl_4 pulse lengths ≥ 400 msec result in SiO_2 deposition that is nearly independent of SiCl_4 pulse length.

The saturation of the SiO_2 deposition at longer SiCl_4 pulse lengths is believed to result from NH_4Cl formation. The NH_4Cl salt forms from the complexation of the HCl reaction product with the NH_3 catalyst. More HCl reaction product and NH_4Cl salt is produced during the longer SiCl_4 pulse lengths. Eventually the NH_4Cl poisons the surface because the NH_4Cl formation rate exceeds the NH_4Cl sublimation rate. The vapor pressure of the NH_4Cl salt varies from 4×10^{-5} Torr at 300 K to 3×10^{-4} Torr at 318K. The problem of

NH₄Cl salt formation does not occur with the Si(NR₂)₄, Si(OH)_a(OR)_{4-a} or SiH_b(OR)_{4-b} silicon precursors that do not contain halogens.

Figure 7 displays the ellipsometric measurements of the SiO₂ film thickness deposited after various numbers of NH₃/SiCl₄ pulses. The H₂O pressure was 300 mTorr and the NH₃ pressure was 100 mTorr. The SiCl₄ pulse length was fixed at 50 msec. The H₂O purged the system for 20 seconds between each NH₃/SiCl₄ pulse. Figure 7 shows that the catalyzed SiO₂ CVD is directly proportional to the number of NH₃/SiCl₄ pulses. The measured SiO₂ CVD rate was 0.24 Å/pulse or 0.72 Å/min at 318 K. The refractive index of these thicker SiO₂ films was determined to be n=1.43 ± 0.03.

The linear increase in the SiO₂ film thickness versus number of NH₃/SiCl₄ pulses indicates that the SiO₂ deposition kinetics remain constant versus time. This behavior argues against permanent NH₄Cl salt formation under these reaction conditions. Salt incorporation could poison the SiO₂ surface and degrade the SiO₂ CVD reaction efficiency. Performing the SiO₂ CVD reaction at 318 K enhances the NH₄Cl sublimation rate and prevents the NH₄Cl salt from impairing the SiO₂ CVD reaction.

Example 5. Surface Properties of SiO₂ films

The surface topography of the SiO₂ films was imaged using a NanoScope III atomic force microscope (AFM) from Digital Instruments operating in tapping mode. The AFM images were collected within 1-2 hours of removing the samples from vacuum to prevent surface contamination by ambient dust particles. Scan lengths of 250 nm - 1.2 μm were performed using a 1.2 μm scanning head. The AFM images were conditioned to remove AFM artifacts using the software provided by Digital Instruments.

Figure 8 displays a side view and top view of a SiO₂ film deposited at 318 K after 500 NH₃/SiCl₄ pulses. The H₂O pressure was 600 mTorr and the NH₃ pressure was 600 mTorr. The SiCl₄ pulse length was fixed at 100 ms. This SiO₂ film had a thickness of ~1000 Å. The surface topography in the AFM image reveals island structures that have grown together and resemble “shingles on a roof”. The root mean square (rms) surface roughness obtained from these AFM images was ± 15 Å. In comparison, the roughness of the initial cleaned Si(100) substrate was ±2 Å (rms).

The observed surface structure in the AFM image suggests that the catalyzed SiO₂ CVD nucleates at various sites on the cleaned Si(100) surface. As the SiO₂ growth

progresses, the individual SiO_2 islands eventually merge with each other. The spatial frequency distribution or power spectral density of the SiO_2 surface topography was compared directly with the initial cleaned Si(100) substrate. The spatial frequencies that comprise the SiO_2 surface topography are weighted more heavily towards lower frequencies or longer wavelengths. This observation is consistent with the larger island features that dominate the surface topography of the catalyzed SiO_2 CVD films.

Example 6. Temperature dependence of SiO_2 films

The temperature dependence of the catalyzed SiO_2 CVD is displayed in Figure 9. The H_2O and NH_3 pressures were 600 mTorr and 150 mTorr, respectively. The SiCl_4 pulse length was fixed at 50 msec. The SiO_2 film thickness deposited by 30 consecutive $\text{NH}_3/\text{SiCl}_4$ pulses decreases as the temperature is increased from 313 K to 333 K. The solid line is shown only to connect the data points and direct the eye. Given the total time required for the 30 $\text{NH}_3/\text{SiCl}_4$ pulses, the SiO_2 deposition rate drops from 7.5 Å/min at 313 K to 0.14 Å/min at 333 K. The reduction in the SiO_2 growth results primarily from the reduction in the SiCl_4 , H_2O and NH_3 coverages at higher temperatures.

The catalyzed SiO_2 CVD exhibits a pronounced decrease with temperature as displayed by Fig. 9. The reduction in SiO_2 growth at higher temperatures is the result of two competing processes. The net reaction rate is controlled by the SiCl_4 , H_2O and NH_3 coverages and the rate at which the SiCl_4 and H_2O reactants are converted to products. The coverage of the reactants and catalyst should exhibit an exponential decrease with temperature. In contrast, the reaction rate should display a exponential increase with temperature. The reduction in the catalyzed SiO_2 CVD rate with increasing temperature indicates that the SiCl_4 , H_2O and NH_3 coverages must dominate the observed SiO_2 growth.

Example 7. Desorption of NH_4Cl

The reaction of the NH_3 catalyst with HCl to form the NH_4Cl salt has important implications for catalyzed SiO_2 CVD when using the silicon precursors containing chlorine. NH_4Cl salt formation can convert the NH_3 catalyst to a chemically inactive form.

The NH_4Cl salt can build up on the SiO_2 surface during long SiCl_4 pulse lengths and degrade the SiO_2 deposition. This NH_4Cl salt formation explains the saturation of the SiO_2 deposition at SiCl_4 pulse lengths > 400 ms in Fig. 6. However, the effect of the NH_4Cl salt can be negligible if NH_4Cl deposition is minimized by pulsing the SiCl_4 reactant and

providing sufficient time for NH₄Cl sublimation between SiCl₄ pulses. To facilitate the removal of the NH₄Cl salt, the SiO₂ surface temperature was maintained slightly above room temperature at 313- 333 K to promote the sublimation of the NH₄Cl salt back to NH₃ and HCl. The desorption rate of NH₄Cl was rapid enough for complete removal of the NH₄Cl salt during the H₂O purge of 20 s between NH₃/SiCl₄ pulses.

The formation of the NH₄Cl salt may also have a beneficial effect on the energetics of catalyzed SiO₂ CVD. The formation of NH₄Cl from HCl and NH₃ is exothermic by 42 kcal/mole. Consequently, NH₄Cl formation provides an enhanced thermodynamic driving force for SiO₂ formation from H₂O and SiCl₄ and may help to reduce the overall reaction activation barrier.

However, NH₄Cl salt formation alone does not explain the entire catalytic effect of the amine bases. NH₃ also has a strong catalytic effect for the silicon precursors such as Si(OR)₄ that do not contain chlorine. This catalytic effect is independent of NH₄Cl salt formation because organosilanes do not produce an HCl reaction product that is necessary to form the NH₄Cl salt.

The method of the present invention can be operated at reaction conditions where NH₄Cl salt formation does not degrade the SiO₂ CVD growth rate. Fig. 7 illustrates that SiO₂ films can easily be deposited at rates of 0.24 Å per NH₃/SiCl₄ pulse or 0.72 Å/min at 318 K. Higher SiO₂ deposition rates of > 16 Å/min can be achieved by varying the SiCl₄, H₂O and NH₃ pressures.

Also, the deposited SiO₂ films are very smooth as revealed by Fig. 8. The SiO₂ films display a surface roughness of only ± 15 Å (rms) for a deposited SiO₂ film thickness of 1000 Å. This minimal surface roughness corroborates that NH₄Cl salt formation does not interfere with the catalyzed SiO₂ growth.

Example 8. SiO₂ film quality and stoichiometry.

Rutherford Backscattering (RBS) experiments were performed on several catalyzed SiO₂ CVD films to evaluate the film quality and stoichiometry. The RBS investigations employed a 2.45 MeV He²⁺ primary ion beam. The backscattered ions were collected from the sample at ~20° off-specular. The H content of the films was also evaluated by collecting the H⁺ ions that were forward-scattered from the SiO₂ film.

The RBS measurements obtained an elemental ratio of 2.1/1 for O/Si. These results

reveal that the deposited film is nearly stoichiometric SiO₂. The N/Si atomic ratio was below the detection threshold of the RBS measurements, i.e. <0.02 %. This small upper limit for N indicates that the NH₃ catalyst is not incorporating into the SiO₂ film when using the SiCl₄ and H₂O reactants.

The RBS analysis also revealed that the Cl/Si atomic ratio was <0.02%. This low ratio is consistent with a complete reaction between the H₂O and SiCl₄ reactants. Modest levels of carbon (~1%) and some heavy metal contaminants were also detected in the SiO₂ films. The carbon impurities probably are derived from small hydrocarbon partial pressures in the deposition chamber that is pumped by a liquid N₂ trapped diffusion pump and operates at a base pressure of 1 x 10⁻⁷ Torr.

Rutherford backscattering (RBS) investigations did not observe any N or Cl contaminants in the SiO₂ films. Thus, although the NH₄Cl may interfere with SiO₂ deposition under some reaction conditions, there is no evidence that NH₄Cl is incorporated in the SiO₂ CVD films. These RBS results argue that the growth temperatures of 313 - 333 K during the SiCl₄ and H₂O reactions were sufficient for complete removal of the NH₄Cl salt from the SiO₂ surface during the H₂O purge.

NH₃ can react with SiCl₄ to form Si₃N₄ under certain conditions. SiCl₄ and NH₃ have also been employed earlier to obtain Si₃N₄ (ALD) using sequential surface reactions. However, the SiCl₄ and NH₃ half-reactions during Si₃N₄ ALD have a negligible rate at T < 700 K. Further, the reaction between SiCl₄ and NH₃ in the gas phase is also inconsequential at room temperature.

In accordance with the present invention, it has been demonstrated that NH₃ can be used as a catalyst for the SiCl₄+2H₂O → SiO₂ + 4HCl and Si(OR)₄+2H₂O → SiO₂ + 4ROH reactions at room temperature. The precursors are inexpensive and widely available. Because the catalyzed process can be used at such low temperatures, it facilitates the use of temperature sensitive substrates such as polymers or biological materials in electronic devices. The catalyzed CVD process in accordance with the present invention may be applied to the growth of other materials.